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RAMAN SPECTROSCOPIC STUDY OF ACETYLENE ON SUPPORTED  
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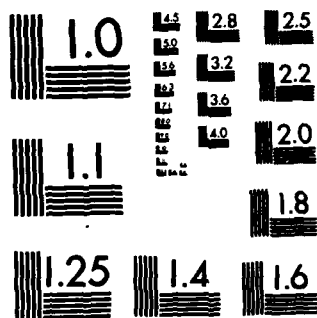
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W. L. Parker, A. R. Siedle and R. M. Hexter

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**Raman Spectroscopic Study of Acetylene on Supported Rhodium Catalysts**

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Abstract

*sigma 2, pi C2H2.*

→ Raman spectra of acetylene on alumina supported rhodium have been measured. Analysis of these spectra indicate that at room temperature and saturation coverage the dominant surface species is  $\sigma_2, \pi \text{ C}_2\text{H}_2$ . This is in striking contrast to the surface species which has been deduced for  $\text{C}_2\text{H}_2$  on the single crystal faces of rhodium at these temperatures. ↗

There exists a relatively large body of experimental observation concerning the interaction of small hydrocarbon molecules with group VIII metals<sup>1,2</sup>. Synthetic chemists have amassed a wealth of data concerning the distribution of reaction products for hydrogenation reactions on these metals which indicate that cis addition to unsaturated adsorbates is predominant<sup>3,4</sup>. This information is to be contrasted with the microscopic information obtained using conventional surface science experimental techniques which have detected surface intermediates not having obvious preference for cis versus trans products<sup>1</sup>. Surface hydrocarbon chemistry has been probed by a wide variety of methods including, electron energy loss spectroscopy (EELS)<sup>5</sup>, low energy electron diffraction (LEED)<sup>6</sup>, secondary ion mass spectrometry (SIMS)<sup>7</sup>, ultraviolet photoelectron spectroscopy (UPS)<sup>8</sup> and near edge X-ray fine structure spectroscopy (NEXAFS)<sup>9</sup>. All of these experimental techniques require ultrahigh vacuum conditions and consequently are not necessarily sensitive to the species of importance under catalytically relevant conditions. Surface sensitive probes which can operate under higher pressures and coverages are clearly desirable. Optical spectroscopies, such as Raman spectroscopy, provide such a probe since photons rather than charged particles interact with the surface, and they are not scattered efficiently by the gas phase. Surface enhanced Raman spectra of organic adsorbates on catalytically important group VIII metals have recently been described<sup>10</sup>. This paper reports enhanced Raman spectra of acetylene on a supported rhodium catalyst and the identification of  $\sigma_{2,\pi}$ -C<sub>2</sub>H<sub>2</sub> (ads) on this surface under conditions in which it has been surmised that C<sub>2</sub>H<sub>2</sub> is present as an alkylidyne species on single crystal rhodium surfaces<sup>1</sup>.

Rhodium supported on high purity alumina was prepared by the hydrogen reduction of rhodium trichloride<sup>11</sup> utilizing a high vacuum combination reactor and Raman cell<sup>10</sup> developed in this laboratory. Reduction occurred at 150°C under 100 torr of H<sub>2</sub>; after reduction the sample temperature was maintained at 150°C with continuous pumping so that a final base pressure of  $5 \times 10^{-7}$  torr was achieved. Following cooling to room temperature, acetylene was admitted to the cell and Raman spectra were obtained with the 4880 Å line of an Ar<sup>+</sup> ion laser. The size distribution of metal crystallites on supported rhodium prepared in this manner has been investigated by electron microscopy. At 10% (wt %) Rh loading the average particle is present as a two-dimensional raft with a diameter of approximately 2.6 nm<sup>12</sup>. Transmission infrared spectroscopy of CO adsorbed on this kind of surface (10% Rh/Al<sub>2</sub>O<sub>3</sub>) yields spectra which greatly resemble those obtained on a Rh(111) surface<sup>13</sup>, indicating that the distribution of adsorption sites, at least for CO, is the same on these two surfaces.

Raman spectra of C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>D<sub>2</sub>, and <sup>13</sup>C<sub>2</sub>H<sub>2</sub> have been measured at room temperature and saturation coverage (47 torr) on alumina supported rhodium. These spectra are presented in Figure 1. Comparison of the vibrational frequencies of C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>D<sub>2</sub> with the observed isotopic shifts of the acetylenic unit in isolated complexes, Table 1, enables us to assign the most intense acetylenic bands at 1481 cm<sup>-1</sup> and 1096 cm<sup>-1</sup>, to C=C stretch and C-H bending modes respectively. This C=C stretch assignment is substantiated by the <sup>13</sup>C isotopic shifts. In the lower frequency region, there is a very small peak at 978 cm<sup>-1</sup> which exhibits an isotopic shift characteristic of a C-H motion<sup>14</sup>. This is tentatively assigned to the antisymmetric bending mode,  $\delta_{CH(as)}$ . By analogy with acetylene adsorbed on single crystal surfaces and the isolated organometallic



complexes  $\text{Os}_3(\text{CO})_{10} \text{C}_2\text{H}_2$  and  $\text{Co}_2(\text{CO})_6 \text{C}_2\text{H}_2$  (Table 2) whose vibrational spectra have been extensively analyzed<sup>15,16,17</sup> these data indicate that the surface species is  $\sigma_2, \pi\text{-C H}$  (see Figure 2). In this, the C-C bond is essentially parallel to the rhodium surface, the C-C-H angle is decreased from the  $180^\circ$  of free acetylene and the C-C bond order is approximately 1.9. Such geometric features have previously been established in the trimetallic diphenylacetylene complex,  $\text{Os}_3(\text{CO})_{10}(\text{PhC}_2\text{Ph})$ ,<sup>18</sup> which serves as an additional plausible molecular model.

If the "surface selection rule" for Raman spectroscopy<sup>19</sup> is valid for small rhodium particles, then the presence of the antisymmetric in-plane bending mode may be used to put limits on the adsorption site symmetry. The maximal site symmetry is  $C_s$ , but this requires that all of the carbon and hydrogen atoms lie in a mirror plane. Such a geometry occurs for the  $\text{C}_2\text{H}_2$  unit in  $\text{Co}_2(\text{CO})_6 \text{C}_2\text{H}_2$  but would be expected to give rise to a more intense CH antisymmetric bending band. The low C-C stretching frequency, less than ethylene, is taken as evidence that the actual bond order is less than 2. This argues for a tilted arrangement to maximize the bonding to a third surface atom. In this tilted orientation the maximum site symmetry would be  $C_1$ . The surface hydrocarbon species observed by Raman spectroscopy is tightly bound since no significant changes in signal intensity or peak position occur on evacuating the cell to  $5 \times 10^{-7}$  torr. It is also chemically active as the spectrum vanishes upon addition of 100 torr of hydrogen at  $150^\circ\text{C}$ .

Stability of the  $\sigma_{2,\pi}$ -C<sub>2</sub>H<sub>2</sub> on supported Rh at 300K is in striking contrast to the facile rearrangement from  $\sigma_{2,\pi}$ -C<sub>2</sub>H<sub>2</sub> to a surface alkylidyne at 270K on bulk, single crystal Rh(111)<sup>1</sup>. The persistence of this surface species at higher temperatures provides a straightforward and logical pathway to the observed cis 1,2 addition of hydrogen or deuterium to the C-C triple bond in alkynes on supported metal catalysts. It is far more challenging to accomodate the established stereo- and regiospecificity of supported metal catalysts in terms of a surface alkylidyne species. At least three mechanisms may account for the difference in surface species on the single crystal and the supported metal.

1) metal-support interactions change the nature of the binding of the adsorbate to the metal.

2) Rearrangement and hydrogen transfer in the adsorbate requires the cooperation of several neighboring sites and these sites are blocked at saturation coverage.

3) the finite size of the metal crystallite leads to changes in the electronic structure of the metal so that the adsorbate binding is fundamentally different.

Experiments are underway with alkyl- and perfluoroalkyl substituted alkynes adsorbed on metal particles in order to elucidate the important factors in the adsorption process.

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TABLE 1. Comparison of Isotope Shifts

$\text{Os}(\text{CO})_{10}\text{C}_2\text{H}_2^*$	$\text{C}_2\text{H}_2$ on 10% Rh/ $\text{Al}_2\text{O}_3$	$\text{Co}_2(\text{CO})_8\text{C}_2\text{H}_2^{**}$	
1.01	1.05	1.04	$\nu_{\text{CC}}^{(\text{H})} \quad \nu_{\text{CC}}^{(\text{D})}$
1.36	1.29	1.27	$\delta_{\text{CH}}^{(\text{s})} \quad \delta_{\text{CD}}^{(\text{s})}$
1.40	1.36	1.19	$\delta_{\text{CH}}^{(\text{as})} \quad \delta_{\text{CD}}^{(\text{as})}$

\* 3 fold site

\*\* 2 fold site

TABLE 2. Comparison of Group Frequencies.

$\Sigma^+_{g, 2H_2}$	$1_{A_u}$	$C_2H_2$ on Pt(111) *	$Os_3(CO)_{10}C_2H_2^{**}$	$Co_2(CO)_6C_2H_2^{***}$	$CH_3C Co_3(CO)_9^+$	$C_2H_2$ on 10% Rh	Assign.
3374	*	3010	2996	3116	2888	*	$\nu_{CH}(s)$
1974	1380	1310	1301	1402	1161	1476	$\nu_{CC}$
3289	3020	*	2945	3086	2930	*	$\nu_{CH}(as)$
612	1049	985	1035	894	1420 1356	1098	$\delta_{CH}(s)$
730	*	*	978	768	1004	981	$\delta_{CH}(as)$
2701	*	2240	2180	2359	*	*	$\nu_{CD}(s)$
1762	1310	1260	1282	1346	1161	1408	$\nu_{CC}$
2439	2215	*	2140	2297	2192	*	$\delta_{CD}(as)$
537	844	730	760	751.4	828 1031	849.2	$\delta_{CD}(as)$
505	*	*	742	602	1002	717	$\delta_{CD}(as)$

# Trans bent geometry

 $\sigma_2, \pi C_2H_2$  $\sigma_2, \pi 3$  fold site $\sigma_2, \pi 2$  fold site

+ Ethylidyne

Figure 1. Raman Spectra of acetylenes on supported rhodium, pressure 47 torr  
laser line = 4880 Å laser power = 200mW, the peaks marked with asterisks  
correspond to combinations of the intense peaks.



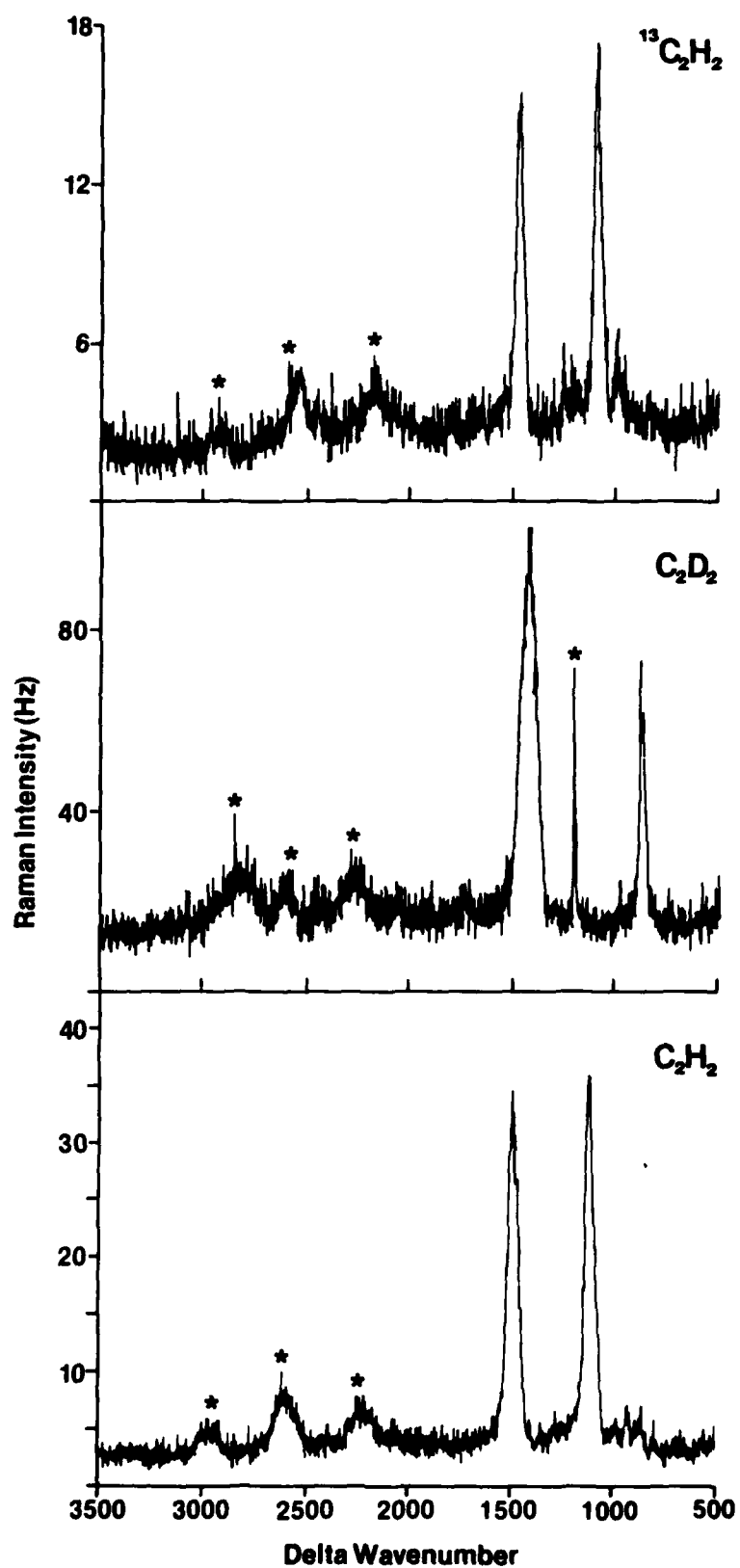
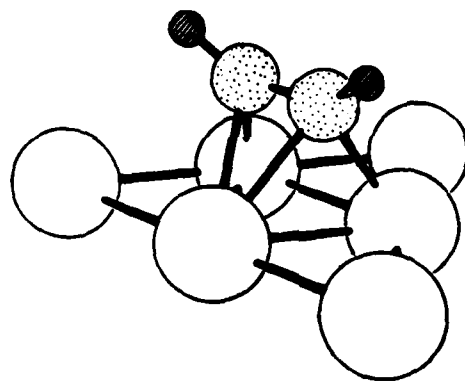


Figure 2. Representation of acetylene bound to a 3 fold site.



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